

10/559 905

## WHAT IS CLAIMED IS:

1. A method comprising the steps of:
  - a) dispersing functionalized CNTs in a solvent to form a dispersion;
  - b) adding epoxy resin to the dispersion to form a mixture;
  - c) removing solvent from the mixture to form a largely solvent-free mixture;
  - d) adding curing agent to the solvent-free mixture; and
  - e) curing the solvent-free mixture to form a CNT-epoxy composite, wherein the CNTs are dispersed and integrated into the epoxy matrix.
2. The method of claim 1, wherein the step of dispersing involves ultrasonication.
3. The method of claim 1, wherein the solvent is selected from the group consisting of aqueous solvents, non-aqueous solvents, and combinations thereof.
4. The method of claim 1, wherein the epoxy resin is selected from the group consisting of DGEBA, Novolac epoxy, cycloaliphatic epoxy, brominated epoxy, and combinations thereof.
5. The method of claim 1, wherein the step of adding comprises a mixing of the mixture components.
6. The method of claim 5, wherein the mixing is carried out with a high-shear mixer.
7. The method of claim 1, wherein the step of removing solvent comprises heating in vacuum.
8. The method of claim 1, wherein the curing agent is selected from the group consisting of cycloaliphatic amines, aliphatic amines, aromatic amines, and combinations thereof.
9. The method of claim 1, wherein the curing agent is added with mixing.

10. The method of claim 1, wherein the functionalized CNTs are fluorinated CNTs.
11. The method of claim 1, wherein the functionalized CNTs are fluorinated SWNTs.
12. The method of claim 1, wherein the CNT-epoxy composite possesses at least one enhanced property selected from the group consisting of mechanical properties, thermal properties, electrical properties, and combinations thereof, relative to the native epoxy.
13. The method of claim 12, wherein such enhanced mechanical properties are selected from the group consisting of an increase in Young's modulus, an increase in the tensile strength, an enhanced elongation-to-break, an enhanced load transfer to the CNTs in the composite, and combinations thereof.
14. The method of claim 1, wherein the functionalized CNTs are made by a process comprising the steps of:
  - a) subjecting CNTs to an oxidizing environment to create end-derivatized CNTs, wherein carboxylic acid groups are present at the ends of the CNTs; and
  - b) fluorinating the end-derivatized CNTs to yield functionalized CNTs with fluorine attached to their sidewalls and carboxylic acid groups attached to their ends.
15. The method of claim 14, wherein the CNTs are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, fullerene tubes, Buckytubes, graphite fibrils, and combinations thereof.
16. The method of claim 14, wherein the CNTs are purified.
17. The method of claim 14, wherein the CNTs are pre-sorted by a property selected from the group consisting of length, diameter, chirality, conductivity, and combinations thereof.

18. The method of claim 14 further comprising a step of reacting the functionalized CNTs, said functionalized CNTs comprising fluorine attached to their sidewalls and carboxylic acid groups attached to their ends, with diamines to yield amino-functionalized CNTs comprising amino groups attached to the CNT sidewalls.
19. The method of claim 14, wherein the functionalized CNTs integrate into an epoxy matrix during curing by forming ester linkages between the carboxylic acid groups attached to the CNT ends and epoxide groups attached to the epoxy resin.
20. The method of claim 14, wherein the functionalized CNTs integrate into an epoxy matrix during curing via bond-forming reactions between the fluorine groups on the CNT sidewalls and diamine curing agents, and further comprising bond-forming reactions between diamines attached on one end to the CNTs and epoxide groups on an epoxy resin at another end.
21. The method of claim 1, wherein the functionalized CNTs are made by a process comprising the steps of:
- a) dispersing CNTs in a solvent to form a dispersion;
  - b) adding an organic acyl peroxide of dicarboxylic acid to the dispersion to form a reaction mixture; and
  - c) heating the reaction mixture to produce free radicals of the type  $\text{HO(O)C-(CH}_2\text{)}_n\cdot$  that subsequently add to the CNT sidewalls to form sidewall carboxylic acid-functionalized CNTs.
22. The method of claim 21, wherein the CNTs are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, fullerene tubes, Buckytubes, graphite fibrils, and combinations thereof.
23. The method of claim 21, wherein the CNTs are purified.
24. The method of claim 21, wherein the CNTs are sorted by a property selected from the group consisting of length, diameter, chirality, conductivity, and combinations thereof.

25. The method of claim 21, wherein the organic acyl peroxide of dicarboxylic acid is selected from the group consisting of succinic acid peroxide, glutaric acid peroxide, and combinations thereof.
26. The method of claim 21 further comprising a step of reacting the sidewall carboxylic acid-functionalized CNTs with a chlorinating agent to form sidewall acyl chloride-functionalized CNTs.
27. The method of claim 26, wherein the chlorinating agent is selected from the group consisting of  $\text{Cl}_2$ ,  $\text{SOCl}_2$ , and combinations thereof.
28. The method of claim 26, further comprising a step of reacting the sidewall acyl chloride-functionalized CNTs with a diamine to form amino-functionalized CNTs.
29. The method of claim 21, wherein the sidewall carboxylic acid-functionalized CNTs integrate into an epoxy matrix during curing by forming ester linkages between the carboxylic acid groups attached to the CNTs and epoxide groups attached to the epoxy resin.
30. The method of claim 26, wherein the sidewall acyl chloride-functionalized CNTs are integrated into an epoxy matrix during curing via bond-forming reactions between the acyl chloride groups on the CNT sidewalls and diamine curing agents.
31. The method of claim 28, wherein the amino-functionalized CNTs are integrated into an epoxy matrix during curing via bond-forming reactions between amino groups attached to the CNTs and epoxide groups attached to the epoxy resin.
32. The method of claim 1, wherein the functionalized CNTs are made by a process comprising the steps of:
- a) reacting CNTs with fluorine to yield fluorinated CNTs;
  - b) dispersing the fluorinated CNTs in a solvent to form a dispersion of fluorinated CNTs;
  - c) reacting a dialcohol with a metal hydroxide to form a metal salt of the dialcohol; and

- d) reacting the metal salt of the dialcohol with the fluorinated CNTs to yield hydroxyl-functionalized CNTs.
33. The method of claim 32 further comprising a step of reacting the hydroxyl-functionalized CNTs with epichlorohydrin to form epoxide-functionalized CNTs.
34. The method of claim 32, wherein the CNTs are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, fullerene tubes, Buckytubes, graphite fibrils, and combinations thereof.
35. The method of claim 32, wherein the CNTs are purified.
36. The method of claim 32, wherein the CNTs are sorted by a property selected from the group consisting of length, diameter, chirality, conductivity, and combinations thereof.
37. The method of claim 32, wherein the dialcohol is bisphenol-A.
38. The method of claim 32, wherein the metal is selected from the group consisting of Li, Na, K, and combinations thereof.
39. The method of claim 33, wherein the epoxide-functionalized CNTs are integrated into an epoxy matrix during curing via bond-forming reactions between amino groups attached to the curing agent.

40. A CNT-epoxy polymer composite made by a method comprising the steps of:
- dispersing functionalized CNTs in a solvent to form a dispersion;
  - adding epoxy resin to the dispersion to form a mixture;
  - removing solvent from the mixture to form a largely solvent-free mixture;
  - adding curing agent to the solvent-free mixture; and
  - curing the solvent-free mixture to form a functionalized CNT-epoxy polymer composite, wherein the functionalized CNTs are dispersed and integrated into the epoxy matrix.
41. The CNT-epoxy polymer composite of claim 40, wherein the functionalized CNTs are integrated into the epoxy matrix via the formation of covalent bonds.
42. The CNT-epoxy polymer composite of claim 40, wherein the step of dispersing involves ultrasonication.
43. The CNT-epoxy polymer composite of claim 40, wherein the solvent is selected from the group consisting of aqueous solvents, non-aqueous solvents, and combinations thereof.
44. The CNT-epoxy polymer composite of claim 40, wherein the epoxy resin is selected from the group consisting of DGEBA, Novolac epoxy, cycloaliphatic epoxy, brominated epoxy, and combinations thereof.
45. The CNT-epoxy polymer composite of claim 40, wherein the step of adding comprises mixing of the mixture components.
46. The CNT-epoxy polymer composite of claim 45, wherein the mixing is carried out with a high-shear mixer.
47. The CNT-epoxy polymer composite of claim 40, wherein the step of removing solvent comprises heating in vacuum.
48. The CNT-epoxy polymer composite of claim 40, wherein the curing agent is selected from the group consisting of cycloaliphatic amines, aliphatic amines, aromatic amines, and combinations thereof.

49. The CNT-epoxy polymer composite of claim 40, wherein the curing agent is added with mixing.
50. The CNT-epoxy polymer composite of claim 40, wherein the functionalized CNTs are fluorinated CNTs.
51. The CNT-epoxy polymer composite of claim 40, wherein the functionalized CNTs are fluorinated SWNTs.
52. The CNT-epoxy polymer composite of claim 40, wherein the CNT-epoxy polymer composite possesses enhanced mechanical properties relative to the native epoxy.
53. The CNT-epoxy polymer composite of claim 52, wherein such enhanced mechanical properties are selected from the group consisting of an increase in Young's modulus, an increase in the tensile strength, an enhanced elongation-to-break, an enhanced load transfer to the CNTs in the composite, and combinations thereof.
54. The CNT-epoxy polymer composite of claim 40, wherein the functionalized CNTs are made by a process comprising the steps of:
- a) subjecting CNTs to an oxidizing environment to create end-derivatized CNTs, wherein carboxylic acid groups are present at the ends of the CNTs; and
  - b) fluorinating the end-derivatized CNTs to yield functionalized CNTs with fluorine attached to their sidewalls and carboxylic acid groups attached to their ends.
55. The CNT-epoxy polymer composite of claim 54, wherein the CNTs are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, fullerene tubes, Buckytubes, graphite fibrils, and combinations thereof.
56. The CNT-epoxy polymer composite of claim 54 further comprising a step of reacting the functionalized CNTs, said functionalized CNTs comprising fluorine attached to their sidewalls and carboxylic acid groups attached to their ends, with

diamines to yield amino-functionalized CNTs comprising amino groups attached to the CNT sidewalls.

57. The CNT-epoxy polymer composite of claim 54, wherein the CNTs integrate into an epoxy matrix during curing by forming ester linkages between the carboxylic acid groups attached to the CNT ends and epoxide groups attached to the epoxy resin.

58. The CNT-epoxy polymer composite of claim 54, wherein the CNTs integrate into an epoxy matrix during curing via bond-forming reactions between the fluorine groups on the CNT sidewalls and diamine curing agents, and further comprising bond-forming reactions between diamines attached on one end to the CNTs and epoxide groups on an epoxy resin at another end.

59. The CNT-epoxy polymer composite of claim 40, wherein the functionalized CNTs are made by a process comprising the steps of:

- a) dispersing CNTs in a solvent to form a dispersion;
- b) adding an organic acyl peroxide of dicarboxylic acid to the dispersion to form a reaction mixture; and
- c) heating the reaction mixture to produce free radicals of the type  $\text{HO(O)C-(CH}_2\text{)}_n\cdot$  that subsequently add to the CNT sidewalls to form sidewall carboxylic acid-functionalized CNTs.

60. The CNT-epoxy polymer composite of claim 59, wherein the CNTs are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, fullerene tubes, Buckytubes, graphite fibrils, and combinations thereof.

61. The CNT-epoxy polymer composite of claim 59 further comprising a step of reacting the sidewall carboxylic acid-functionalized CNTs with a chlorinating agent to form sidewall acyl chloride-functionalized CNTs.

62. The CNT-epoxy polymer composite of claim 61, further comprising a step of reacting the sidewall acyl chloride-functionalized CNTs with a diamine to form amino-functionalized CNTs.



63. The CNT-epoxy polymer composite of claim 59, wherein the sidewall carboxylic acid-functionalized CNTs integrate into an epoxy matrix during curing by forming ester linkages between the carboxylic acid groups attached to the CNTs and epoxide groups attached to the epoxy resin.
64. The CNT-epoxy polymer composite of claim 61, wherein the sidewall acyl chloride-functionalized CNTs are integrated into an epoxy matrix during curing via bond-forming reactions between the acyl chloride groups on the CNT sidewalls and diamine curing agents.
65. The CNT-epoxy polymer composite of claim 62, wherein the amino-functionalized CNTs are integrated into an epoxy matrix during curing via bond-forming reactions between amino groups attached to the CNTs and epoxide groups attached to the epoxy resin.
66. The CNT-epoxy polymer composite of claim 40, wherein the functionalized CNTs are made by a process comprising the steps of:
- a) reacting CNTs with fluorine to yield fluorinated CNTs;
  - b) dispersing the fluorinated CNTs in a solvent to form a dispersion of fluorinated CNTs;
  - c) reacting a dialcohol with a metal hydroxide to form a metal salt of the dialcohol; and
  - d) reacting the metal salt of the dialcohol with the fluorinated CNTs to yield hydroxyl-functionalized CNTs.
67. The CNT-epoxy polymer composite of claim 66 further comprising a step of reacting the hydroxyl-functionalized CNTs with epichlorohydrin to form epoxide-functionalized CNTs.
68. The CNT-epoxy polymer composite of claim 66, wherein the CNTs are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, fullerene tubes, Buckytubes, graphite fibrils, and combinations thereof.
69. The CNT-epoxy polymer composite of claim 66, wherein the dialcohol is bisphenol-A.

70. The CNT-epoxy polymer composite of claim 66, wherein the epoxide-functionalized CNTs are integrated into an epoxy matrix during curing via bond-forming reactions between amino groups attached to the curing agent.

71. The CNT-epoxy polymer composite of claim 40 further comprising at least one additive selected from the group consisting of inhibitors, curing agents, viscosity modifiers, anti-degradation species, colorants, nanoparticles, nanoclays, and combinations thereof.

72. The CNT-epoxy polymer composite of claim 40 further comprising a fiber reinforcement selected from the group consisting of fiberglass, carbon fiber, graphite fabric, KEVLAR, and combinations thereof.

73. A method comprising the steps of:

- a) applying solvent-dispersed CNTs onto a fibrous surface to form an overcoated fibrous material;
- b) removing the solvent to form a CNT-fibrous material composite; and
- c) coating the CNT-fibrous material composite with a polymeric species to form a CNT-enhanced FRP composite.

74. ~~73.~~ The method of claim 72, wherein the CNTs are functionalized.

75. ~~74.~~ The method of claim 72, wherein the CNTs are SWNTs.

76. ~~75.~~ The method of claim 72, wherein the CNTs are dispersed in a solvent selected from the group consisting of alcohols, DMF, ODCB, toluene, THF, and combinations thereof.

77. ~~76.~~ The method of claim 72, wherein the step of applying involves a technique selected from the group consisting of spraying, incipient wetting, immersing, and combinations thereof.

78. ~~77.~~ The method of claim 72, wherein the fibrous material is selected from the group consisting of fiberglass, carbon fiber, graphite fabric, KEVLAR, and combinations thereof.

79. ~~78.~~ The method of claim 72, wherein the solvent is removed by an evaporative means.

80. ~~79.~~ The method of claim 72, wherein the step of coating involves a FRP composites processing technique selected from the group consisting of lay-up, compressing molding, prepreg, autoclave, conventional resin transfer molding (RTM) and its derivative processing techniques such as vacuum assisted resin transfer molding (VARTM).

81. ~~80.~~ The method of claim 72, wherein the polymeric species is selected from the group consisting of an epoxy, vinyl ester, bismaleimide resin, and combinations thereof.

82.  
81.

The method of claim 72, wherein the polymeric species is an epoxy resin that is subsequently cured subsequent to the step of coating.

83.  
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The method of claim 73, wherein the functionalized CNTs comprise functional groups that permit their covalent integration into epoxy matrices.

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~~83.~~ A CNT-enhanced FRP composite comprising:

- a) a fibrous material;
- b) CNTs; and
- c) a polymer matrix.

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~~84.~~ The CNT-enhanced FRP composite of claim 83, wherein the fibrous material is selected from the group consisting of fiberglass, carbon fiber, graphite fabric, KEVLAR, and combinations thereof.

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~~85.~~ The CNT-enhanced FRP composite of claim 83, wherein the CNTs are SWNTs.

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~~86.~~ The CNT-enhanced FRP composite of claim 83, wherein the CNTs are functionalized.

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~~87.~~ The CNT-enhanced FRP composite of claim 83, wherein the polymer matrix is selected from the group consisting of an epoxy, vinyl ester, bismaleimide resin, and combinations thereof.

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~~88.~~ The CNT-enhanced FRP composite of claim 83, wherein the polymer matrix is an epoxy.

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~~89.~~ The CNT-enhanced FRP composite of claim 86, wherein the functionalized CNTs are covalently integrated with the polymer matrix.

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~~90.~~ The CNT-enhanced FRP composite of claim 89, wherein the functionalized CNTs are functionalized SWNTs and the polymer matrix is an epoxy.